

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to the Isomerisation of Paraffin Wax

We, NAAMLooZE VENNOOTSCHAP DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ, of 30, Carel van Bylandtlaan, The Hague, The Netherlands, a company organised under the laws of The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for isomerising paraffin wax and, in particular, to the production of lubricating oil and isoparaffin wax thereby.

Paraffin wax is a normally solid, wax-like substance composed of high molecular weight hydrocarbons. It is usually obtained from the heavier fractions of petroleum such as are used for the production of lubricating oils and certain burning oils. In general, the presence of paraffin wax in such oils is undesirable and it is removed by so-called dewaxing methods during refining. Although paraffin wax is extensively used for many purposes, for example, in the production of waxed paper and water-proofed cartons, there is still a considerable amount of paraffin wax for which there is no ready market.

It is known that the melting points of the hydrocarbons present in paraffin wax are lowered upon conversion to isomers having a more branched structure. Thus, normal hexacosane, a typical wax constituent, is a waxy solid having a melting point of 56° C., whereas its isomer 6:6-dipentyl hexadecane is a normally liquid compound having a melting point of -40° C. Thus, by suitable isomerisation a substantial conversion of high molecular weight paraffin wax to a normally liquid product may be obtained.

The main difficulty to be overcome in

the isomerisation of paraffin wax is the excessive degradation or cracking to lower molecular weight products of little value which generally occurs. It is well known that the tendency for hydrocarbons to crack increases rapidly with increasing molecular weight and this applies whether the cracking occurs under the influence of heat or of a catalyst. Thus, whereas normal butane may be selectively converted to isobutane, the selective isomerisation of paraffins of higher molecular weight becomes increasingly difficult as the molecular weight is increased.

The present invention provides a process for isomerising paraffin wax to products of substantially the same molecular weight without appreciable degradation or cracking, whereby good yields of excellent lubricating oil and isoparaffin wax are obtained. This process comprises vaporising a paraffin wax and contacting the vapours, mixed with at least one mole of hydrogen per mole of said wax and in the absence of any liquid phase with a supported platinum catalyst at a temperature between 300° and 550° C.

The process of the invention may be used to isomerise any normally solid paraffin wax. The wax may be derived from mineral sources, such as petroleum oil, shale, oil from tar sands, gilsonite and ozokerite, from coal by extraction and/or hydrogenation, or may be formed by the Fischer-Tropsch synthesis or as a by-product of other processes. The process of the invention may be used to isomerise crude so-called slack wax or refined waxes of various melting points. While the various crude waxes and refined waxes differ somewhat in properties, e.g. melting point and hardness, they are all composed of hydrocarbons containing

long paraffinic chains. In some paraffin waxes the chains may be slightly branched and some may have naphthenic or aromatic groups attached. Olefinic groups are rarely present but even if present, they do not affect the operation of the process. The paraffin chains of all such wax molecules can be isomerised by the process of the invention to give a product having a more highly branched structure.

The platinum catalyst employed in the process of the invention is supported on any of the conventional carrier materials hitherto employed as supports for platinum catalysts. Alumina is a preferred support material, activated alumina (gamma alumina) and activated bauxite being particularly suitable. The alumina should be substantially free from alkaline substances and particularly from compounds of the alkali and alkaline earth metals. In order to ensure the absence of any appreciable amounts of such materials in the catalyst, it may be necessary to treat the carrier material with acid, e.g. hydrogen chloride or hydrogen fluoride, prior to incorporating the platinum. The amount of platinum in the catalyst may vary from a few hundredths of a per cent, e.g. 0.05%, to about 1%, and is preferably between about 0.1% and about 0.6%.

The platinum may be applied to the support in any one of the several known ways. One suitable method is to impregnate the support material with a solution of a platinum salt, followed by drying and reducing in the conventional manner. Thus pellets of activated alumina may be soaked in a solution of chloroplatinic acid, dried, and reduced in hydrogen at 475° C.

An essential feature of the process of the invention is that the isomerisation is carried out in the presence of a large amount of hydrogen. The mole ratio of hydrogen to hydrocarbon should be at least 1 and preferably above 5 and may be much higher. However, in practice, the ratio will rarely exceed about 300.

In carrying out the process, the wax is vaporised in a suitable vaporiser, mixed with the hydrogen and the mixture is passed into contact with the catalyst. The hydrogen may advantageously be passed through the vaporiser to aid in the vaporisation. The contact is most conveniently effected by supporting a bed of the catalyst in a reaction tube and passing the vapour mixture through the bed. Other methods of contact may, however, be employed if desired. The vapours issuing from the reaction tube are cooled to condense the product and any gas present

is then separated from the condensate and recycled. By repeated recycling of this gas, the hydrogen becomes increasingly diluted with inert gases produced by the minor amount of side reactions occurring in the process. This is not particularly harmful as long as the specified minimum amount of hydrogen is present. In order to prevent the hydrogen from becoming excessively diluted with inert gases, a small amount of the effluent gas may be continuously withdrawn and fresh hydrogen added to the recycle gas.

The temperature in the catalyst bed in the process of the invention is preferably between 375° C. and 490° C. The operation may be carried out under reduced pressure, at atmospheric pressure, or at elevated pressures. Pressures between 3.5 and 210 atmospheres are suitable. Pressures of the order of 21 to 70 atmospheres being generally preferred.

The conditions under which the process of the invention is carried out are such as to retain all the reaction mixture in the vapour phase and avoid any condensation to the liquid phase. It is essential that no condensation to a liquid takes place in the reaction zone.

A contact time of the vapour mixture with the catalyst of only a tenth of a second is in general sufficient to afford a practical conversion. It is evident that with such rates a small reactor is capable of handling a large throughput. Longer contact times may, however, be used, particularly when operating at the lower temperatures. However, the contact time at any given temperature should not be so long as to cause excessive cracking. The contact time may be adjusted between 0.5 and 25 seconds in any case to afford the desired conversion while limiting the formation of cracked products to below 25% and preferably to below about 20%.

When a paraffin wax is isomerised according to the process of the invention under the conditions described above, the product consists of normally liquid oil, unconverted wax, partially converted wax (isoparaffin wax), and a small amount of cracked products. The small amount of cracked material present in the reaction product may be distilled from the oil and wax. Depending upon the nature of the initial paraffin wax and the degree of conversion, the total reaction product or the reaction product from which the cracked products have been removed by distillation may vary in consistency from a slurry or mush to a grease-like or plastic material. This product may be used without any further processing, but for some purposes, particularly where a

crude wax feed was used, it may be desirable to refine the product by such methods as extraction, clay treating or chemical treatment.

5 It will generally be desirable to separate the reaction product into two or more fractions. Thus, by employing conventional dewaxing techniques, a very high quality lubricating oil fraction may be separated. The pour point of the oil will depend in part upon the dewaxing conditions used and in turn the yield will depend in part upon the pour point chosen. Excellent yields of very low pour point oil of adequate viscosity for commercial usage and having a high viscosity index have been obtained from the product of a single pass isomerisation treatment. In view of its very low pour point and very high viscosity index, the oil is particularly suited for many special purposes such, for example, as refrigerator lubricating oil, low temperature hydraulic fluid and in the production of low temperature greases.

The wax residue obtained after separating the oil consists of unconverted and partially converted wax and the mixture has a lower melting point and softer consistency than the starting material. It may be used as such or recycled in the isomerisation process to produce additional amounts of oil.

35 This waxy residue may also be separated by known techniques into a fraction of partially converted or isoparaffin wax and a fraction of unconverted wax. Either of these fractions may be recycled. Isoparaffin wax produced by the partial isomerisation of a wax consisting essentially of normal paraffins partakes somewhat of the characteristics of microcrystalline wax and may be used in place of microcrystalline wax. The isoparaffin wax differs from ordinary paraffin wax in having a much less brittle and more rubbery or plastic consistency. It resembles carnauba wax in its ability to absorb considerable quantities of oil without becoming sticky or tacky.

The amounts of oil, isoparaffin wax and

unconverted paraffin wax present in the reaction product depends somewhat upon the character of the wax feed and largely upon the severity of the treating conditions, i.e. on the degree of conversion attained. When the process of the invention is operated under relatively mild conditions, only a small amount of oil is formed; under more severe conditions the amount of oil is greatly increased, usually with more cracking.

The following examples illustrate the invention.

EXAMPLE I.

A paraffin wax having the following properties was isomerised by the process of the invention:—

Melting point, 59/60° C.
Average Molecular Weight 385

d_4^{20}	0.78
n_D at 60° C.	1.4356
n_D at 70° C.	1.4325
n_D at 80° C.	1.4293

The isomerisation was effected by vaporising the wax with from 52 to 63 moles of hydrogen per mole of wax and passing the vapour mixture through a bed of platinum-alumina catalyst containing 0.3% platinum under the following reaction conditions:—

Temperature	430° C.
Pressure	35 atmospheres
Space Velocity*	25.4

* Space velocity is the volume of wax processed per volume of catalyst per hour.

The losses, including the small amount of cracked products, amounted to about 2.4% of the wax feed. The product was refined by a series of dewaxing steps to separate narrow fractions of the oil present. The amounts and properties of the oil fractions are shown in the following table:

Fraction	Yield (Wt. % of wax feed)	Viscosity cs.		Viscosity Index	Pour Point °C. (ASTM)	n_D at 70° C.
		37.7°C.	99°C.			
A	5.6	12.02	3.16	144	—26	1.4332
B	1.8	12.50	3.00	105	—15	1.4474
C	2.2	11.34	3.15	160	—4	1.4325
D	5.6	11.79	3.29	169	+15.5	1.4322
Total	15.0					

Since the conditions were in this case very mild due to the very high space velocity, (calculated contact time, 0.77 seconds) the degree of conversion obtained was relatively small. It will be noted, however, that 15% by weight of the wax was converted to oil of which about 37% was an oil (fraction A) having a viscosity suitable for low temperature applications, a viscosity index above 100, and a pour point of below -20°C . This desirable oil could be separated and the remaining oil recycled with or without the unconverted and partially converted

wax. Operation under such conditions is attractive because the throughput is high and the losses to cracking are low.

EXAMPLE II.

A further sample of the paraffin wax employed in Example I was isomerised under conditions similar to those in Example I except that the space velocity was 6.8. The losses, including losses to cracked products, amounted to about 5.6% by weight. The product was refined as in Example I to give the following oil fractions:

Fraction	Yield (Wt. % of wax feed)	Viscosity cs. 37.7°C.	Viscosity cs. 99°C.	Viscosity Index	Pour Point °C. (ASTM)	n_D at 70° C.
A	25.4	11.62	3.03	134	-48	1.4330
B	5.3	8.03	2.28	105	-29	1.4460
C	10.7	11.30	3.12	154	-15	1.4317
D	13.7	11.75	3.27	163	+18	1.4315
	Total 55.1					

It will be seen that by employing somewhat more severe isomerisation conditions, the yield of oil was increased to 55% by weight and that more than half of the oil was lubricating oil of especially desirable properties. The unconverted and partially converted wax, amounting to 39% of the feed, could be recycled.

EXAMPLE III.

A further sample of the paraffin wax

employed in Example I was isomerised under conditions similar to those in Example I but with a space velocity of 2.3. Under these more severe conditions the losses, including the loss through cracked products, amounted to about 18% by weight. The product was refined as in Example I to give the following yields of oil.

Fraction	Yield (Wt. % of wax feed)	Viscosity cs. 37.7°C.	Viscosity cs. 99°C.	Viscosity Index	Pour Point °C. (ASTM)	n_D at 70° C.
A	6.6	6.55	1.95	89	-57	1.4551
B	37.8	11.01	2.89	127	-51	1.4326
C	10.7	11.01	3.04	152	-12	1.4312
D	9.8	11.10	3.14	164	+7	1.4310

It will be seen that the yield of valuable lubricating oil was again greatly increased with a relatively small increase in cracked products.

The above examples illustrate on a readily comparable basis the effect of the severity of the conditions upon the yields obtained. The severity of the conditions may also be altered by changing other factors than the space velocity, e.g., the temperature and/or pressure.

EXAMPLE IV.

A white, hard, heavy distillate wax having the following inspection data was isomerised:

Melting Point, A.S.T.M.—87	72° C.
Gravity A.P.I., 99° C.	51.8
n_D at 80° C.	1.4376
Oil content, A.S.T.M. D—721	0.87%
Molecular Weight	522
Viscosity, SSU at 99° C.	50.6

The wax was vaporised and isomerised under the following conditions:

Temperature, °C.	404—440
Pressure	17.5 atmospheres
Space Velocity	5.12
Mole ratio of hydrogen to wax	33

There were obtained 74.5% by weight of a wax of soft consistency containing lubricating oil; 12.4% by weight of a distillate fraction boiling between 150° C. and 265° C. at 6.9 mm. pressure and containing light lubricating oil; 9.4% by weight of cracked products boiling up to 150° C. at 6.9 mm. pressure and 3.7% by weight of gas plus experimental loss.

EXAMPLE V.

Bright stock wax is the very high molecular weight wax obtained by dewaxing bright stock, which is the residue remaining after distilling off the lubricating oil fractions from a lubricating oil petroleum stock. A bright stock wax having the following inspection data was isomerised:—

Density, g/ml. at 20° C	0.8899
Viscosity at 99° C A.S.T.M.	
D—445	20.50
Molecular weight	717

The wax was vaporised with hydrogen and isomerised under the following conditions:—

Temperature, °C	418—421
Pressure, p.s.i.g.	300
Space Velocity	1.66
Mole ratio of hydrogen to wax	336

There were obtained 71.9% of a very soft wax containing bright stock; 20.8% of a distillate fraction boiling up to 288° C. at 8 mm. pressure and containing lubricating oil; and 7.3% of gas plus unaccounted losses. The soft wax was found to have a lower coefficient of friction than the starting wax and in view of its softer consistency was a better lubricant for metal rolling.

What we claim is:—

1. A process for the isomerisation of paraffin wax, which comprises vaporising a paraffin wax and contacting the vapours, mixed with at least one mole of hydrogen per mole of said wax and in the absence of any liquid phase, with a supported platinum catalyst at a temperature

between 300° C. and 550° C

2. A process as claimed in claim 1 wherein the vaporised wax is mixed with at least 5 moles of hydrogen per mole of wax.

3. A process as claimed in claims 1 or 2 wherein the carrier for the platinum catalyst is alumina free from alkaline substances.

4. A process as claimed in any one of the preceding claims wherein the temperature is between 375° C. and 490° C.

5. A process as claimed in any one of the preceding claims wherein the pressure is between 3.5 and 210 atmospheres.

6. A process as claimed in claim 5 wherein the pressure is between 21 and 70 atmospheres.

7. A process as claimed in any one of the preceding claims wherein the contact time of the mixture of vaporised wax and hydrogen with the catalyst is between 0.5 and 25 seconds and is insufficient to produce more than 25% conversion to cracked products.

8. A process as claimed in any of the preceding claims wherein the hydrogen is used mixed with inert gases.

9. A process as claimed in any one of the preceding claims wherein the reaction product is distilled to remove normally liquid byproducts formed by cracking.

10. A process as claimed in claim 9 wherein the residue remaining after removing the byproducts is dewaxed to separate a lubricating oil of low pour point and high viscosity index from a waxy residue.

11. A process as claimed in claim 10 wherein the waxy residue is separated into isoparaffin wax and unconverted paraffin wax.

12. A process for preparing a lubricating oil of low pour point and high viscosity index and isoparaffin wax by isomerising paraffin wax substantially as hereinbefore described with reference to the Examples.

13. Lubricating oil of low pour point and high viscosity index and isoparaffin wax prepared by isomerising paraffin wax by a process claimed in any one of the preceding claims.

14. Lubricating oil as claimed in claim 13 having a pour point below -20° C. and a viscosity index above 100.

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